JURES 2022

Precise characterization of low temperature structures of vanadium oxides

Jose Angel Silva Guillén

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EXCELENCIA SEVERO OCHOA

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EXCELENCIA SEVERO OCHOA

- Non-profit Foundation funded by the regional Government of Madrid and the Ministry of Science and Education of Spain in 2008
- Severo Ochoa Center of Excellence
- 210 researchers – 34.5 years average age
- Annual expenditure > 11M€ (65% of the budget from external competitive sources)

Secure, clean and efficient energy

P1: Multifuctional Nanomaterials, Energy Harvesting, Catalysis, Sensors & Devices
P5: Ultrafast time-resolved spectroscopies

Health, demographic change & wellbeing

P3: Nanomedicine for Neurological, Oncological & Infection deseases

P7: Technology Translational Platform

P4: Nanomagentism & spin-resoved spectroscopy
P6: Critical Raw Materials & processes

Climate action & raw materials

P2: Fundamental properties of **2D Materials and Quantum Devices**

Security

Adapted from Dr. Manuela Garnica

THEORY

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Universidad de Oviedo
Universidá d'Uviéu
University of Oviedo

Víctor M. García Suárez

EXPERIMENT

Universidad de Oviedo
Universidá d'Uviéu
University of Oviedo

Pablo Alonso González

Javier Martín Sánchez

THEORY

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Víctor M. García Suárez

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CFM
Materialen Fisika Zentroa
Materials Physics Center
Centro de Física de Materiales

EXPERIMENT

Universidad de Oviedo
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Pablo Alonso González

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Disclaimer!!

- On going project!!
  - Not many (preliminary) results (yet)
  - Some theory…
- Goals:
  - Study the low temperature structure of intercalated V_2O_5
  - Give theoretical support to the experimental node

V_2O_5

- Applications
  - Sensors
  - Photocatalysts
  - Electrochromic devices
  - Lithium-ion batteries

- Low cost
- Abundance

V_2O_5

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  - Sensors
  - Photocatalysts
  - Electrochromic devices
  - Lithium-ion batteries

- Low cost
- Abundance

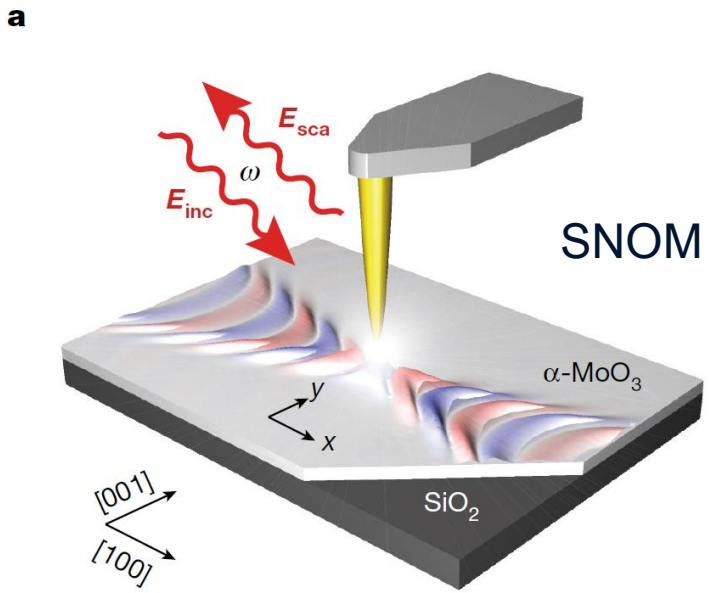
- Novel Applications
  - Optical: Phonon polaritons

V_2O_5

- Novel Applications
  - Optical: Phonon polaritons

    (light coupled to optical phonons)

- Confine light
- Nanolasers
- Infrared detectors
- Molecular sensors
- …
- Basically no tuning



Nature **562**, 557 (2018)

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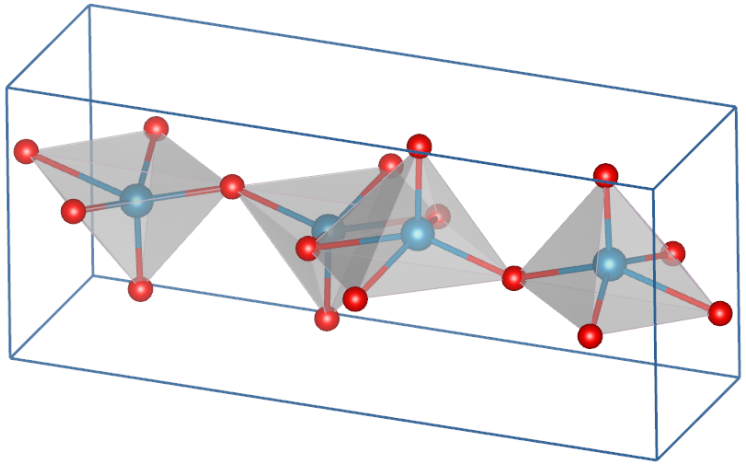
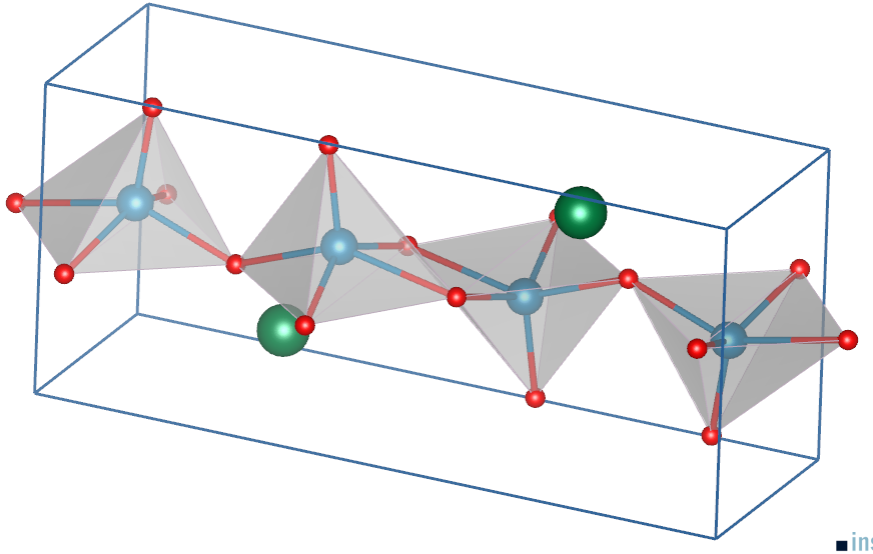
V_2O_5

- Structure
  - Orthorhombic structure
  - Inequivalent O positions → Asymmetric bonds
  - van der Waals material
  - It can be easily doped (Na, Ca, Li)





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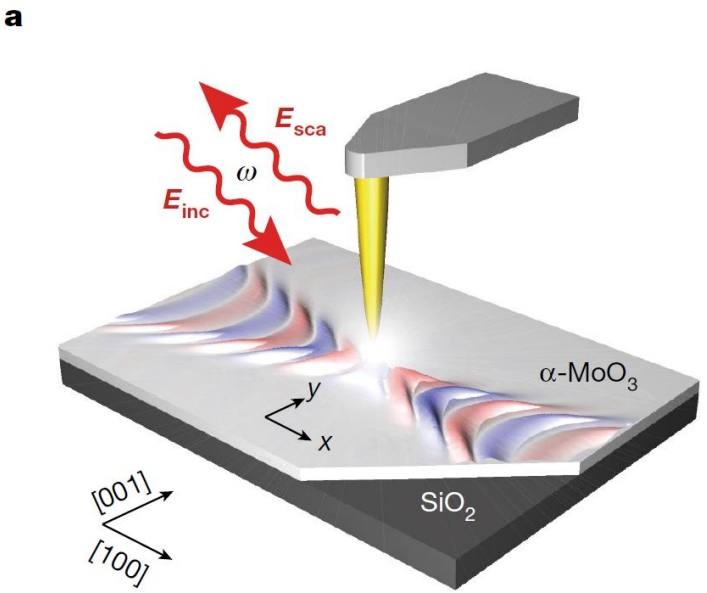
V_2O_5 - doping

- Novel Applications
  - Optoelectronic: Phonon polaritons
    (light coupled to optical phonons)

- Confine light
- Nanolasers
- Infrared detectors
- Molecular sensors
- …
- Some tuning



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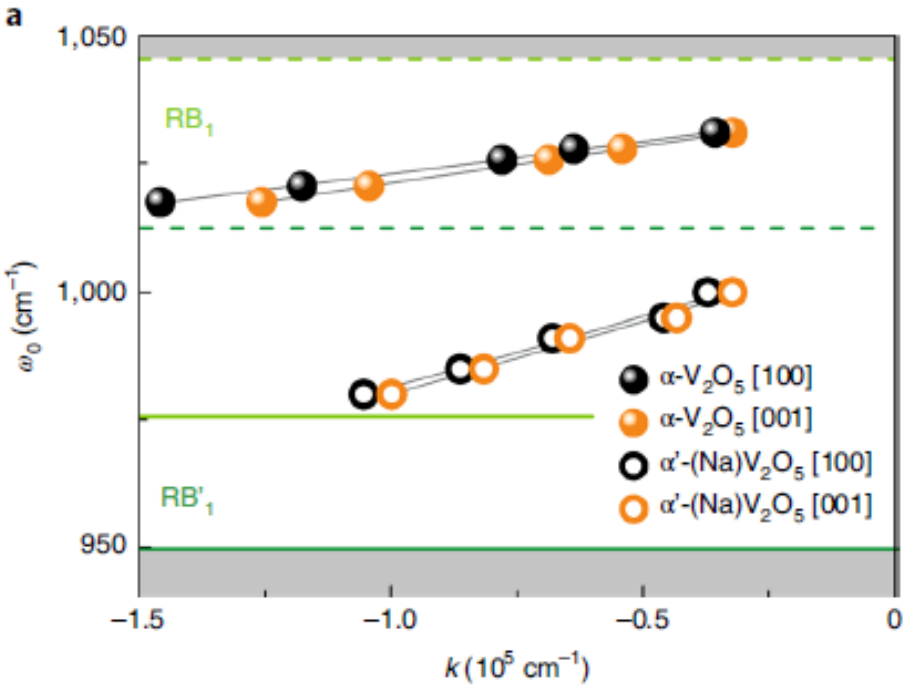

Nature Materials
19, 964 (2020)

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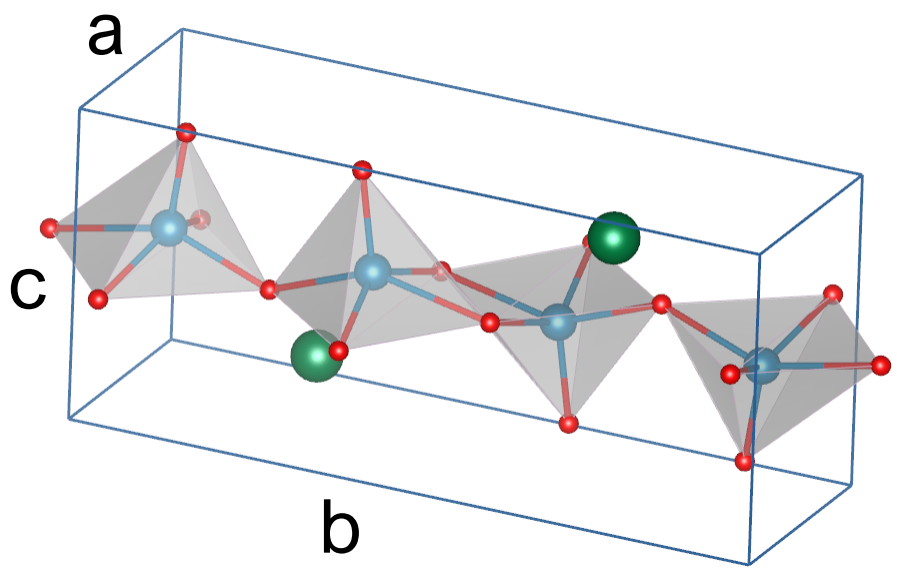
NaV_2O_5

- Structure
  - Lowering the temperature ⟹ Structural transition



Solid State Communications **112**, 397 (1999)
Monoclinic P2/b
2a×2b×4c

Phys. Rev. Lett. **82**, 3633 (1999)
Orthorhombic Fmm2
2a×2b×4c

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J. Phys. Soc. Jpn. **71**, 385 (2002).
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NaV_2O_5

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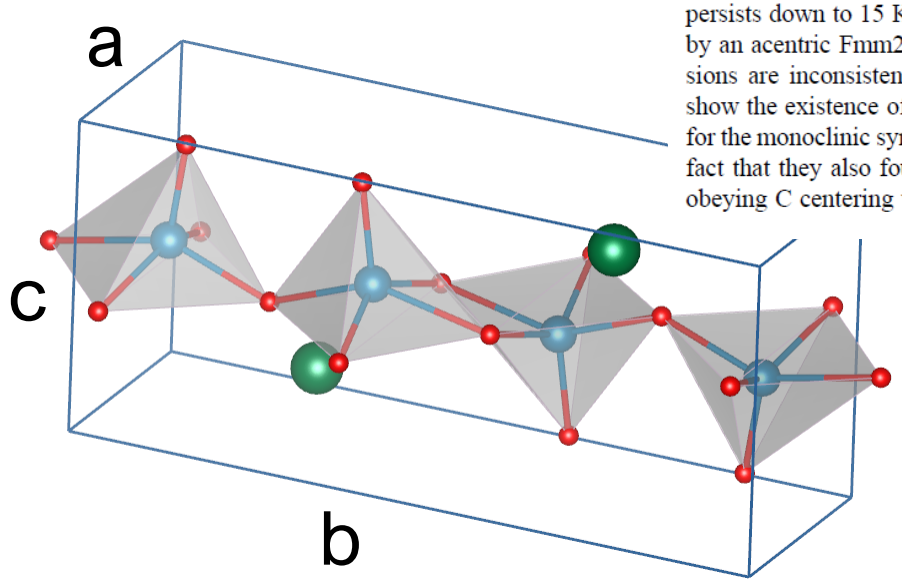

Note added: After completion of this work an analysis of the low-temperature NaV_2O_5 crystal structure, using synchrotron radiation X-ray diffraction, appeared in [20]. The authors found that a centrosymmetric average structure persists down to 15 K, with a modulation pattern described by an acentric Fmm2 superstructure. However, the conclusions are inconsistent with our optical data which clearly show the existence of Raman tensors that are characteristic for the monoclinic symmetry. The explanation may lie in the fact that they also found a few reflections in X-ray spectra obeying C centering which they did not consider in detail.

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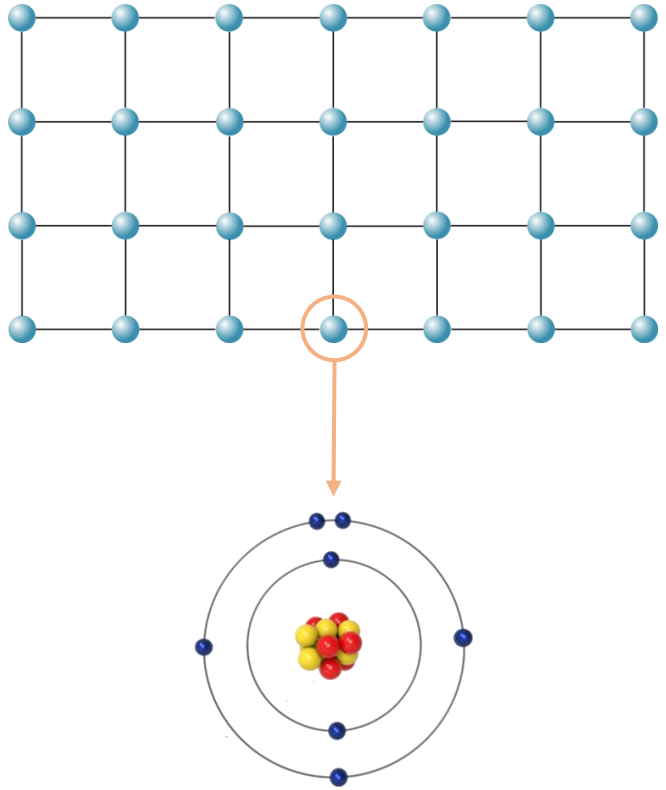
How?

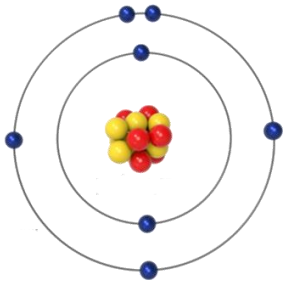
- Condensed matter problem

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN} + V_{ext}$$



How?



- Approximations
  - Born-Oppenheimer (adiabatic) approximation:
    - The mass of the electron is much smaller than that of the nuclei ($m_{e^-} <<< m_n$)

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN} + V_{ext}$$

$$\Psi(\mathbf{r},\mathbf{R}) = \varphi_{ni}(\mathbf{R})\,\Phi_i(\mathbf{r},\mathbf{R})$$

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + V_{ext}$$

$$\hat{H}_e\Phi_i(\mathbf{r},\mathbf{R}) = E_i[\mathbf{R}]\,\Phi_i(\mathbf{r},\mathbf{R})$$

$$\left[\hat{T}_N + \hat{V}_{NN} + E_{e_i}[\mathbf{R}]\right]\varphi_{ni}(\mathbf{R}) = E_{ni}\varphi_{ni}(\mathbf{R})$$

How?

$$\hat{H}_e \Phi_i (\mathbf{r}, \mathbf{R}) = E_i [\mathbf{R}] \Phi_i (\mathbf{r}, \mathbf{R})$$

- Density Functional Theory
  - Theory to handle correlated many body problems
  - Hohenberg-Kohn theorems:
    - Any property of the ground state system can be described as a functional of the ground state electron density
    - We transform our 3N variable problem to a 3 variable problem with the electron density!
  - Kohn-Sham approach: Made the theory useful
    - Auxiliary non-interacting system
    - Group all many-body effects in an exchange-correlation potential (V_{xc})
      - LDA
      - GGA
      - …

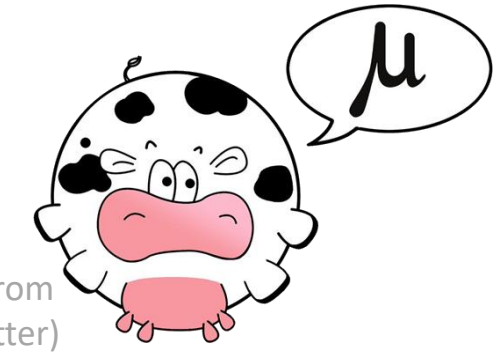


Image taken from @shedka (Twitter)

How?

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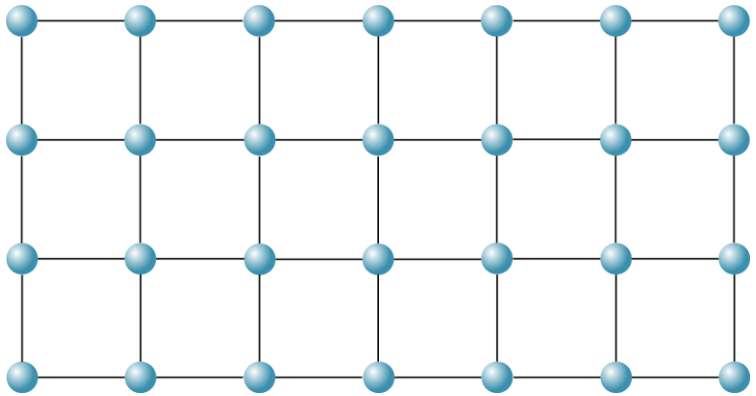
How?

$$\left[\hat{T}_N + \underbrace{\hat{V}_{NN} + E_{e_i}[\mathbf{R}]}_{V(\mathbf{R})}\right]\varphi_{ni}(\mathbf{R}) = E_{ni}\varphi_{ni}(\mathbf{R})$$

- Phonons
  - Born-Oppenheimer approximation: Still a many body problem.
  - The atoms will have small displacements from their equilibrium position compared to the interatomic distances.
  - Born-Oppenheimer potential: $V(\mathbf{R}) = V(\mathbf{R_0}) + V_1(\mathbf{R}) + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \ldots$



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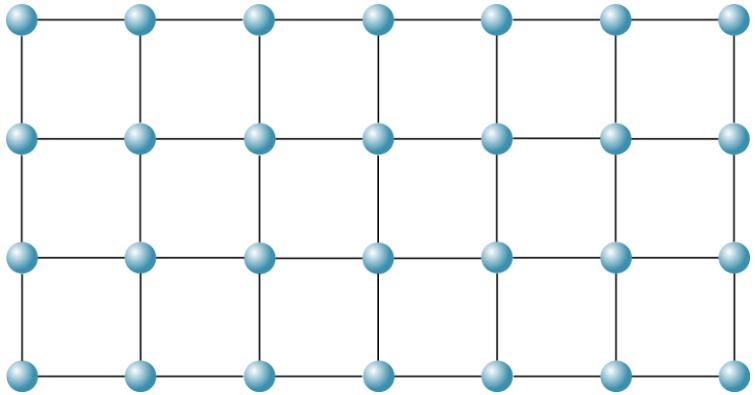
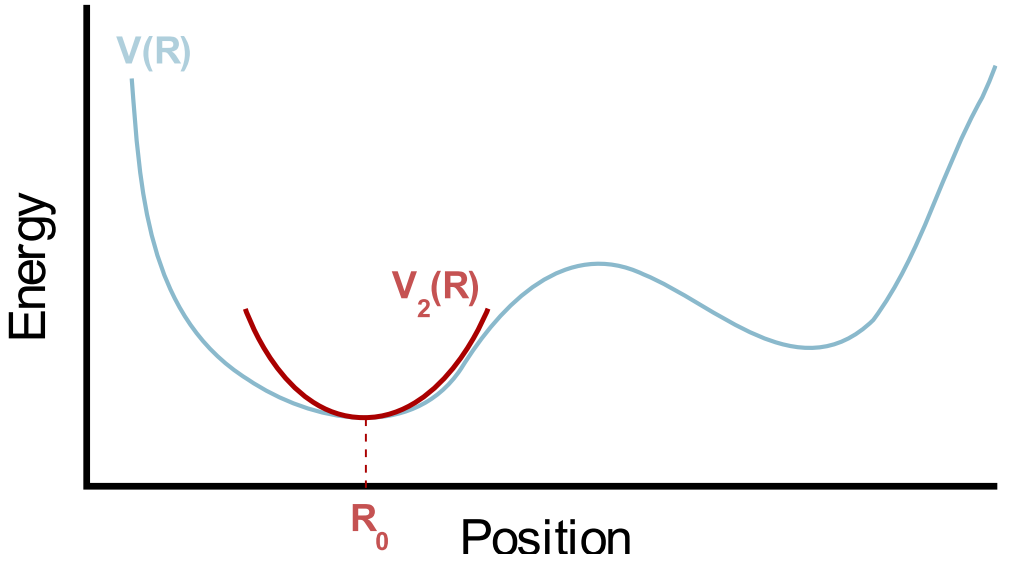
  - Harmonic approximation + Classical atomic forces: Newton equation!





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  - Calculation of the force constants:
    - By “finite displacements” (i.e. Siesta).
    - By “perturbation methods” (i.e. Quantum-Espresso).

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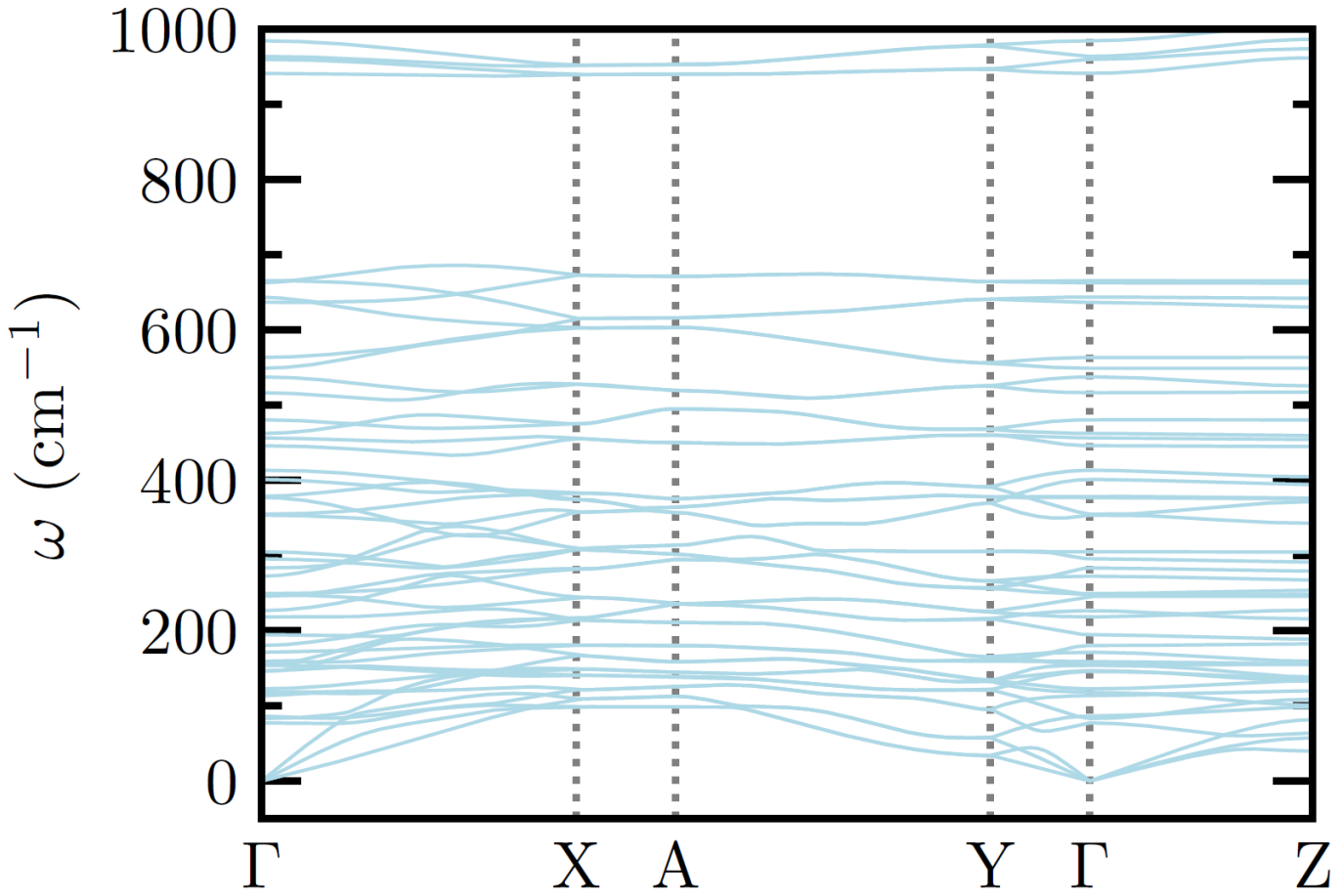
Atoms = ~~Quantum~~ particles

~~Temperature~~

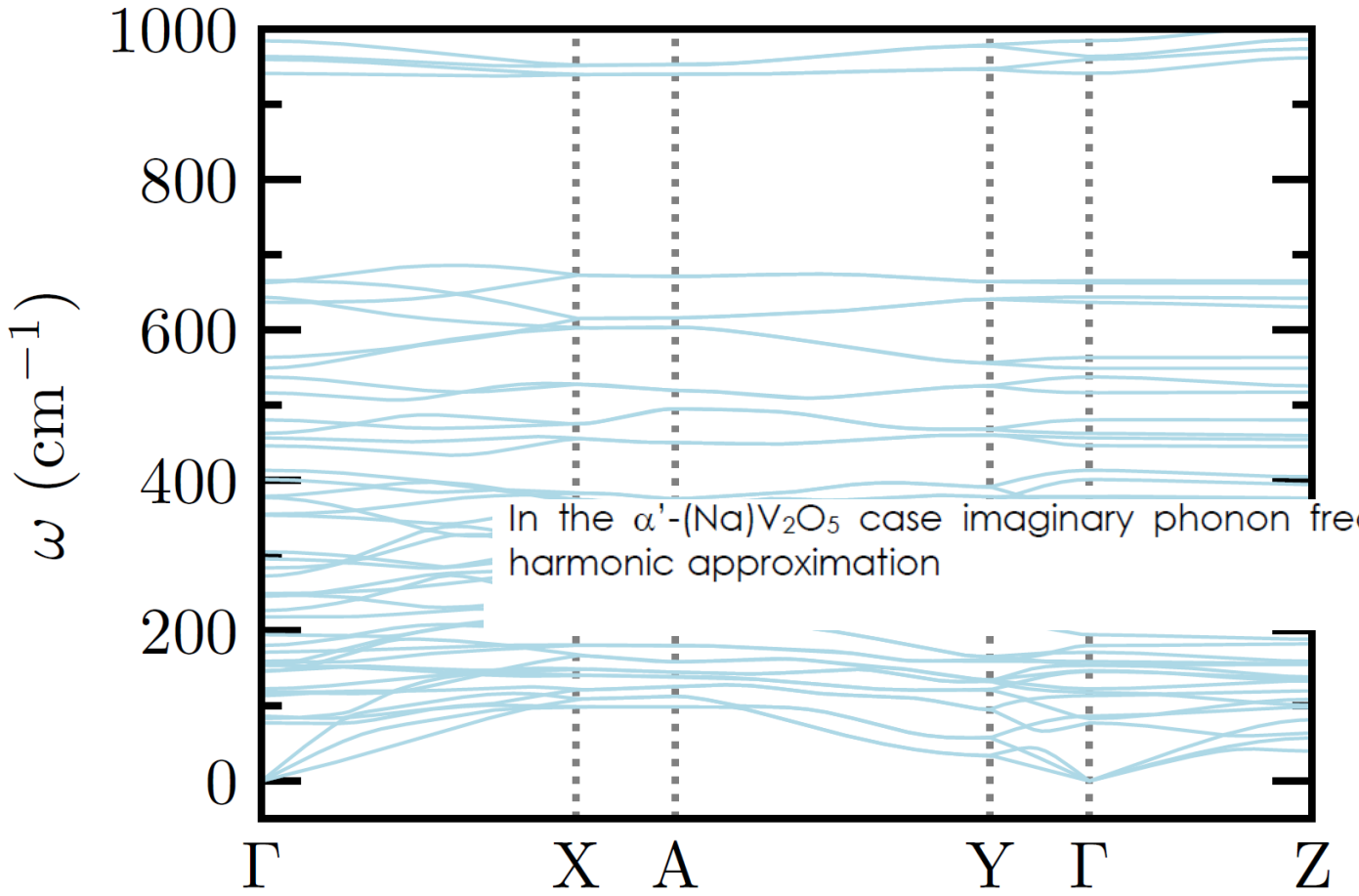
Typical approach

- Electronic calculation
  - Optimization of the comp. parameters (40 calculations max)
    - Energy cutoff: 140.0 Ry
    - K-points: 16×6×15
  - Optimization of the lattice and the atom's position (1 calculation)
  - Electronic band structure, DOS …
- Phonon calculation
  - The electronic calculation has to be very well converged (forces)
  - q-points: 2×1×2 (4 calculations, each q can be calculated separately)
- Total comp. time: 55 Khours (each q ~ 9 days).

Typical approach



Typical approach



In the α'-(Na)V_2O_5 case imaginary phonon frequencies are found within the harmonic approximation

Nature Materials
19, 964 (2020)

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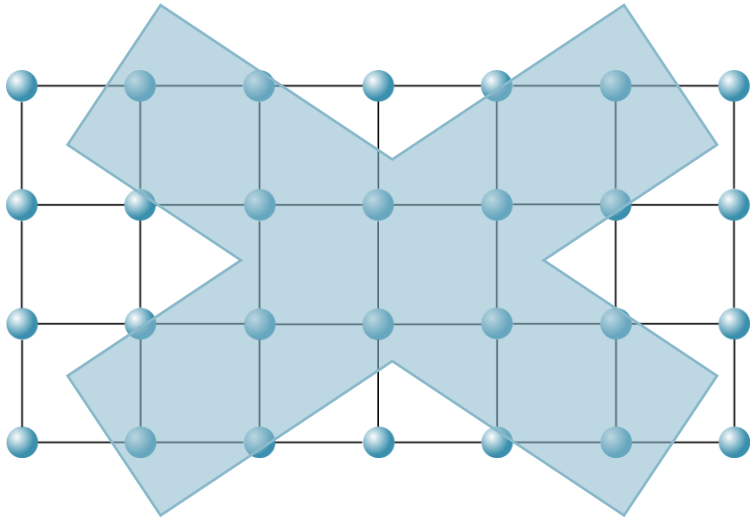
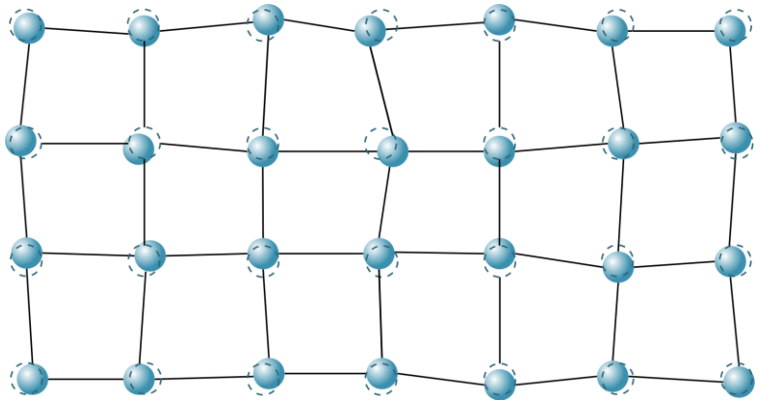
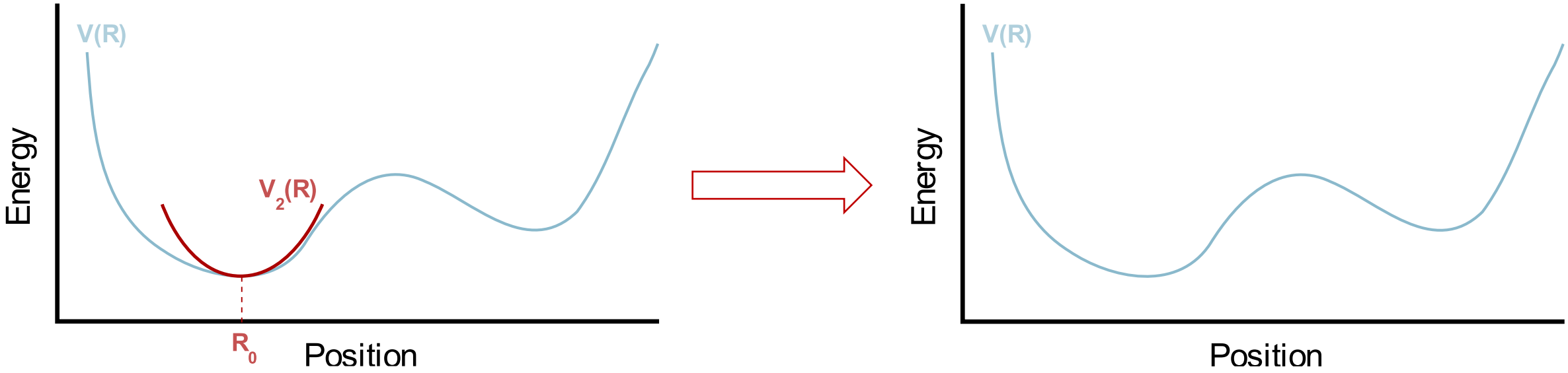




How?

- Phonons beyond the harmonic approximation:
  - $\left[\hat{T}_N + \underbrace{\hat{V}_{NN} + E_{e_i}[\mathbf{R}]}_{V(\mathbf{R})}\right] \varphi_{ni}(\mathbf{R}) = E_{ni}\varphi_{ni}(\mathbf{R})$
  - The BO potential is still a many body problem.
  - Method to incorporate ionic quantum and anharmonic effects without approximating V(**R**).

SSCHA
Stochastic Self-Consistent Harmonic Approximation
sscha.eu



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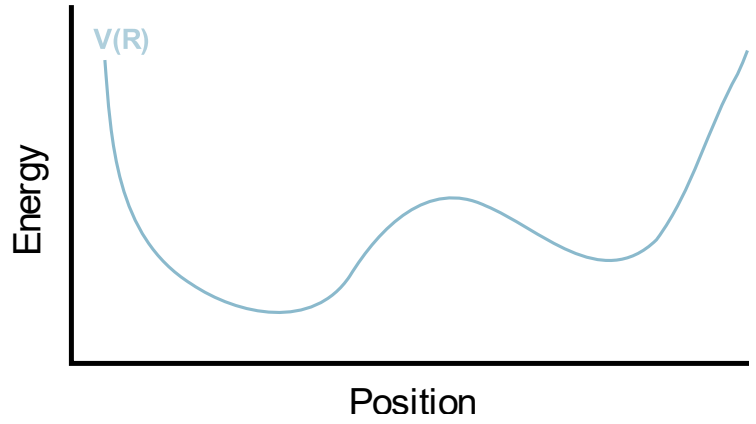
  - The BO potential is still a many body problem.
  - Method to incorporate ionic quantum and anharmonic effects without approximating V(**R**).
  - Variational principle: $\mathcal{F}[\rho] = \langle T_i + V \rangle_\rho - TS[\rho] \geq F$
  - Quantum and thermal fluctuations of ions.
  - Stochastic nature: Monte Carlo evaluations.

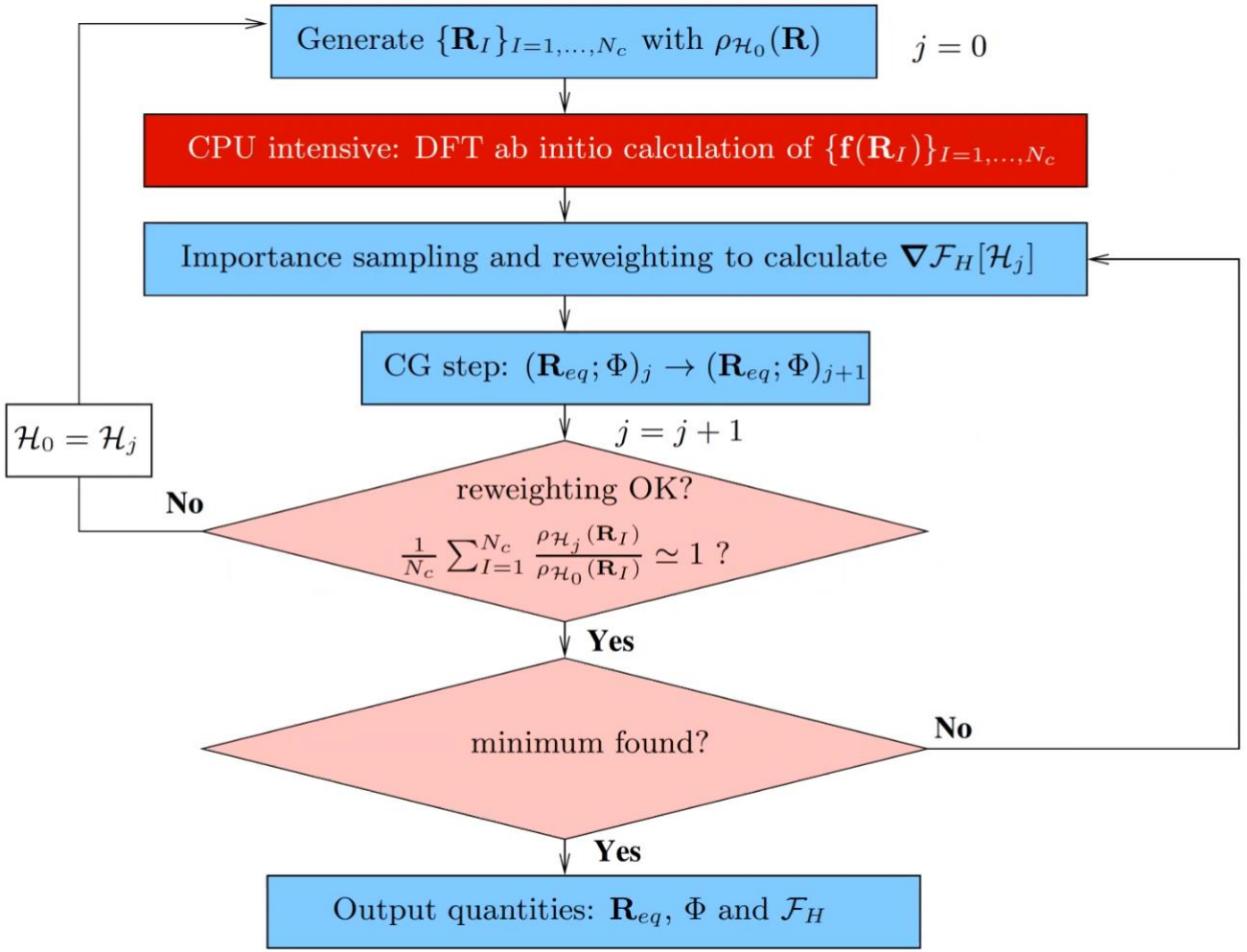
SSCHA
Stochastic Self-Consistent Harmonic Approximation
sscha.eu



J. Phys.: Condens. Matter **33**, 363001 (2021)

Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation
https://cfm.ehu.es/errealab/teaching/

How?



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Details

- 2x1x2 supercell (64 atoms)
  - Around 900 structures
  - Energy cutoff: 140.0 Ry
  - K-points: 8×6×8
  - 48 processors (high-memory nodes) – 16 hours

- Total comp. time: 700 Khours.

For each temperature!

SSCHA
Stochastic Self-Consistent Harmonic Approximation
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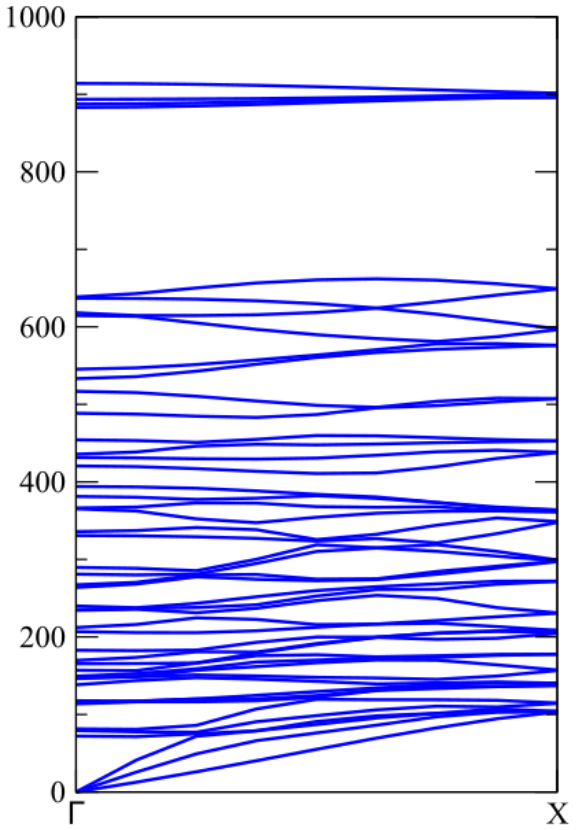
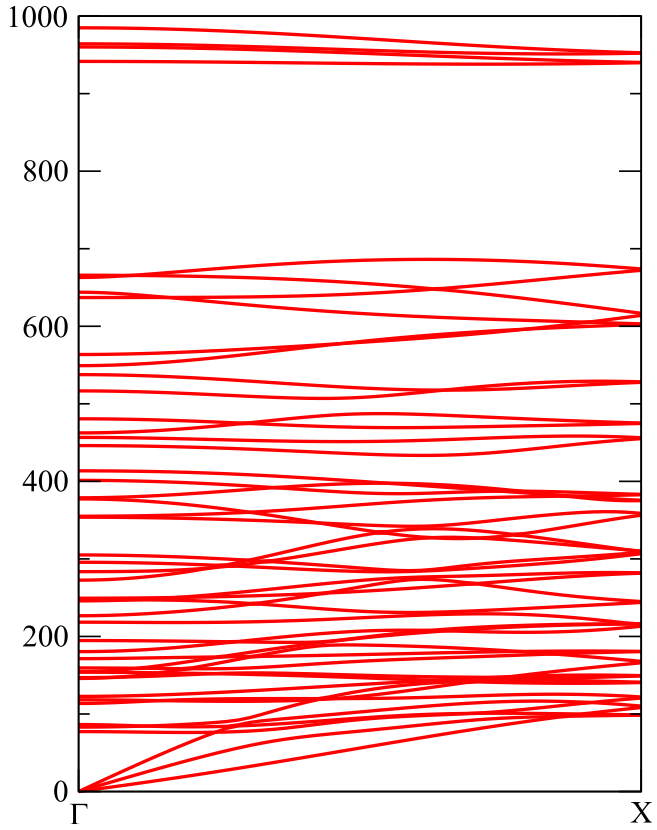
Results



SSCHA
Stochastic Self-Consistent Harmonic Approximation

T=300 K



Harmonic

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Conclusions & outlook

- NaV_2O_5 is an interesting material for theory and experiment
- Harmonic calculations are relatively easy to perform.
- In order to calculate the temperature dependence of the system we need to go beyond the harmonic approximation.
- SSCHA is a very complete method, but very demanding
- We need an HPC facility to perform these calculations

- Soon (before the end of this activity):
  - Phonon dependence with temperature (finishing the calculations a.t.m.)
  - Most stable structure at low temperatures

Thanks to…

and…
you for your attention!